Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A THERMOCHEMICAL ANALYSIS OF THE REACTION BETWEEN ALUM AND POTASSIUM HYDRATE.

By A. V. E. Young.

Communicated by the Corresponding Secretary, June 10, 1885.

PART I.

In the course of a thermochemical study of potassic aluminate I desired to use as one element of calculation the amount of heat evolved in the following reaction,

$$Al_2(SO_4)_3 . K_2SO_4 + 6\ KOH = 4\ K_2SO_4 + Al_2(OH)_6,$$

assuming in accordance with Thomsen's statement that the alum is equivalent, for this purpose at least, to aluminic sulphate. This quantity is given by Thomsen* as 30528 calories. He determines it directly by precipitation with potassic hydrate in the calorimeter, and, as a control, determines the heat of precipitation with three molecules of baric hydrate. The results of the two methods agree fairly well. This value is made by the same author the basis for the indirect determination of the formation heat of the chloride and several other compounds of aluminum, and this, notwithstanding the fact that he notes the complete precipitation of the aluminic oxide by five molecules of potassic hydrate instead of six, which would appear to indicate the formation of a basic precipitate. He evidently assumes that the addition of six molecules of the hydrate leaves the precipitate free of sulphuric acid, and that the agreement with the result obtained when baric hydrate is used affords confirmation of the assumption. Indeed, in other instances, e. g. sulphates of copper, cobalt, and cadmium, when the two methods do not give concordant results, he adopts the result by baric hydrate, and rejects that by potassic hydrate as being untrustworthy by reason of the formation of a basic precipitate. It would seem unsafe to assume, without experimental verification, that baric hydrate may not produce a basic precipitate as well as potassic hydrate, and thus render both methods open to the same objection.

---

* See Thermochemische Untersuchungen, i. 366.

However this may be, the results which I obtained soon led to the suspicion that the reaction with potassic hydrate was not so simple as is indicated by the above equation. One question after another arising which I was unable to answer, I have been led step by step to what may be called a thermochemical analysis of the reaction in question. The first part of the results obtained constitutes the substance of the following paper. At a later date, I hope to publish a determination of the precipitation heat of aluminic hydrate by a method free from these objections. The first series of experiments involves the determination of the reaction heat of alum and potassic hydrate, the proportion of the latter present varying from .5 to 10 molecules. This is followed by a parallel series determining the composition of the precipitates obtained in the calorimetric experiments. Before considering in detail the results of the first series, I give a brief description of the calorimetric methods and of the calculations that were used.

METHOD AND CALCULATIONS.

The general method of heat measurement is that described by Berthelot. The calorimeter used was made after the specifications given by him* without essential variation. The inner platinum calorimeter has a capacity of somewhat more than 1,200 c.c. The stirrer is a simple one, a piece of platinum foil fused to a glass rod. The thermometers were made by Baudin of Paris especially for thermochemical work after specifications by Berthelot,† and were calibrated by Pernet at the Bureau International des Poids et Mesures. The zero points have been recently redetermined. The three pairs of duplicates taken together give a range of temperature from 0° to 33° C. They are graduated to fiftieths of a degree, and the readings were made, usually with the aid of a small hand lens, to $\frac{1}{200}$ of a degree, and often to $\frac{1}{400}$. The experiments were performed in a large basement room without artificial heat, where, during a portion of the year at least, the temperature conditions were fairly satisfactory. The operation consisted, with but one or two exceptions, in mixing in the calorimeter two portions of liquid of 500 c.c. For this measurement two flasks were used, their graduation being verified by weight.

Solutions containing the requisite quantity of constituents were prepared, diluted to somewhat less than 500 c.c., and allowed to stand in closed flasks beside the calorimeter until the following day, or perhaps during a longer interval. When ready for the calorimetric determination one of the prepared solutions was transferred with rinsing to the measuring-flask, (care being taken not to change unduly its temperature in the handling,) and filled to 500 c.c. with distilled water that had stood a day or longer on the same table. It was then poured into the calorimeter and its temperature taken, after thorough stirring, at intervals of five minutes. The change of temperature during this interval should not be more than .02°. At the same time, the second solution having been transferred to the second measuring-flask, its temperature in the flask was taken by a second thermometer in similar manner. Its change likewise should not be more than .02° per interval of five minutes; and it is also important that it should be close to that of the room, which was read from an ordinary thermometer.

---

* Essai de Mécanique Chimique, i. 140.

† Ibid., p. 164.

When the temperature conditions were satisfactory, and the readings duly recorded, the contents of the second flask were poured as quickly as possible into the calorimeter, the mixture thoroughly stirred, and the resultant temperature recorded. The interval between the last reading of the initial temperatures and the first of the resultant temperature was in this series of experiments one and a half or two minutes, and with few exceptions the maximum temperature was reached in this time. Readings were then taken, always with stirring, every minute for about five minutes, and then at an interval of five minutes, in order to have a record of the rate of cooling.

There seems to be one unsatisfactory point in this method of manipulation; namely, the difficulty of obtaining the true temperature of the second volume of liquid while it still remains in the flask, and of transferring it to the calorimeter without consequent change. Experience will convince one of this difficulty in experiments where a variation of .01° is of considerable importance. My habit is to close the flask and shake it as thoroughly as possible before inserting the thermometer, and to see that its temperature at the time shall be such that it need not be left more than five or ten minutes before transferring to the calorimeter. Meantime the flask stands in a loose bag of flannel, supported by a frame that serves as handle so that the hand itself is distant several inches from the flask. Nevertheless, I have not infrequently obtained apparently accidental results, which varied from the mean notably more than the average variation, and of which the difficulty just described seems the probable cause. I hope later on to reduce, if not to eliminate, this uncertainty by a simple modification of apparatus.

Calculations. — The unit of heat employed, the calorie, is the quantity required to raise one kilogramme of water one degree at the temperature of the experiment. The mean temperature after mixing is calculated by the following formula:

$$T_m = \frac{(A + d)\,T_a + B\,(T_b - t)}{A + d + B};$$

in which

T_m = mean temperature.
A = water equivalent in grammes of solution A in calorimeter.
d = water equivalent in grammes of calorimeter, stirrer, and thermometer.
B = water equivalent in grammes of solution B.
T_a = observed initial temperature of solution A in calorimeter.
T_b = observed initial temperature of solution B in flask.
t = correction in degrees to make the reading of the two thermometers correspond.

The temperatures T_a and T_b, recorded in the tables, are those actually observed. In the calculation of T_m the correction d is used, but no correction is made for difference between the observed zero and the actual zero, as it would not affect the final result. The temperature recorded as T_c is the difference between the calculated mean temperature and the resultant temperature; in other words, the change of temperature due to the reaction, and is positive unless otherwise specified.

The column f in the tables gives the factor by which T_c is multiplied to reduce the heat disturbance of the reaction in calories to molecular proportions, and H is this final result. The factor f is obtained as follows:

$$f = (A + B + d) \times \frac{\text{mol. wt.}}{\text{grms. taken}} \text{ (of alum).}$$

In all the experiments of this paper the water equivalent of the calorimeter and its belongings is 8.5 grm., while A and B are the volumes in cubic centimeters of the constituent solutions reckoned as grammes of water (Berthelot's method of calculation[*]), each numerically equal to 500 c.c. unless otherwise specified. $t = .008°$.

Limit of Error. — The reading of temperature is by far the most considerable element limiting the certainty of experimental observation. The quantity of alum used, 20.667 grm., is weighed to one part in more than twenty thousand. The KOH solution is titrated against oxalic acid, and its titration confirmed gravimetrically. The quantity used in an experiment varied from 10.67 c.c. to over 200 c.c. This was measured in a burette to .05 c.c., which would make the maximum variation considerably less than one per cent of the quantity measured, even when the latter was at its minimum. Whereas, if we put the limit of temperature reading at .005°, and consider that the change in temperature depends upon three separate readings, the maximum of error should be .01°, or .005° putting the limit of reading at .0025°. This would be a very large per-cent variation in many of the experiments when the quantity measured falls considerably below 1°. Inspection of the tabulated data will show that in many cases the observed variation of T_c is much smaller than the calculated maximum; e. g. the first six experiments of Table I., where it is only .001°. In most of the experiments a variation of .005° in T_c makes a variation of .24 Cal. in H.

---

[*] Essai de Mécanique Chimique, i. 190.

SERIES I.

The numerical data of these experiments are recorded in Table I. The alum used was the commercial article, well crystallized and free of iron. Of it 20.067 grm. were used in each experiment, and the solution prepared as already described. The proportion of water was about 2,600 molecules to one of alum; in Thomsen's experiments, 2,400. In column h is recorded the rate of heat disturbance per molecule of KOH. The results H and h are seen graphically expressed in Plate I., where x is the number of molecules of KOH added, and y in Line I. represents H, in Line III., $h \times 10$.

Inspection of Line I. shows that the heat evolution increases with the quantity of KOH, reaching a maximum at $x = 6$ or 6.5, and from this point diminishes until $x = 10$, when the re-solution of the precipitate in the excess of KOH is complete. This means that the solution of the precipitate in excess of KOH is accompanied by heat absorption, or is endothermic. It will be shown farther on that the addition of KOH beyond $x = 8.5$ causes no further heat disturbance, and that 8.13 mol. KOH completely redissolve the precipitate; hence, in constructing the line, the value of y at $x = 8.13$ is made the same as at $x = 10$.

Line III. reveals still more. It shows a constant rate of heat evolution per molecule of KOH from $x = .5$ to $x = 1$. At this point it drops abruptly. Now in the analytical part it will be shown (see Plate II. Line V.) that precipitation begins between $x = 1$ and

$x = 1.5$, probably at $x = 1.13$. Hence, in constructing Line III. the minimum is put hypothetically at $x = 1.13$, instead of at $x = 1.5$ which is the point actually determined. Inasmuch as the precipitate at first produced redissolves in excess of alum up to $x = 1.13$, the drop in the line at this point indicates probably that this re-solution also is accompanied by heat absorption. This will be evident upon considering that the heat disturbance, h, is a positive resultant, made up of both positive and negative elements. The principal positive element is the formation heat of potassic sulphate, and since this in all probability remains approximately constant for equal portions of KOH entering into combination, it follows that the negative element increases at the point $x = 1.13$ in consequence of precipitation. In other words, precipitation is accompanied by heat evolution, and resolution of the precipitate by heat absorption.*

Beyond $x = 1.13$ there is evidently a tendency to rise slightly up to $x = 5$, or thereabouts. The break at $x = 4.8$ is within the limit of error, since the larger value recorded in Table I. gives the alternative point, $x = 4.8$, just above the line as seen in the plate. Indeed, the increase between $x = 1.13$ and $x = 5$ depends upon differences which lie so close to the limit of experimental error that one must hesitate to consider it more than probable. It would be interesting to establish it beyond doubt, in view of the analytical results shown in Plate II., Line VII. There can be no doubt, however, that the line drops beyond $x = 5.12$, as would be expected.

It is to be noted that the maximum in Line I. occurs at $x = 6$ or 6.5; while in Line III. it occurs at $x = 5$, which is the point at which the aluminic oxide is completely precipitated. This leads to the question, What causes the continued heat evolution after the precipitation is total? the discussion of which must be deferred until the analytical results have been described. The three experiments recorded in Table III. serve, however, to fix one point bearing thereon. 4.8 mol. KOH were added to one of alum in the usual conditions. Then to this mixture were added in the calorimeter the remaining 1.2 mol. KOH, in the proportionate quantity of water, and the heat evolution measured. The results are fairly satisfactory, considering that the necessary conditions of the experiments were not the best for calorimetric measurement. They serve to show, at least, that the continued evolution of heat between $x = 4.8$ and $x = 6$, in Series I., may be accounted for by the action of the 1.2 mol. KOH on the precipitate formed by the 4.8 mol. A previous experiment, made by adding KOH in the calorimeter to the liquid portion of the mixture 1 alum + 5 KOH (the precipitate being removed), gave zero for a result.

---

* See similar case of lead, Thomsen, i. 377.

SERIES II.

In the second series of experiments the same quantity of alum was dissolved, 10 mol. KOH added, and the whole made up to 500 c.c., as in Series I. To this was added in the calorimeter 500 c c. of sulphuric acid solution, containing of H_2SO_4 quantities varying from .5 to 3 molecules. The numerical data are recorded in Table II. It will be seen that the rate of heat disturbance per molecule of H_2SO_4 is practically constant for $n = .5$ and $n = .75$, but increases at $n = 1$; the first precipitation by neutralization of KOH occurs between $n = .75$ and $n = 1$. The rate then increases to $n = 2.2$, when it again drops. Instead of expressing these direct results graphically, I have calculated from them (at least from Exp. 42–48) the corresponding points in the Lines I. and III. The possibility of this calculation will be apparent from considering that *H* in Series II. is the formation heat of potassic sulphate plus or minus the heat disturbance involved in separating the equivalent potassic hydrate from whatever form of combination it may be in before the addition of sulphuric acid. If we assume that the *n* mol. H_2SO_4 (from $n = 1.5$ to $n = 2.2$) are converted into K_2SO_4, and count the formation heat of the latter as a known quantity, we have the means of calculating indirectly the values of *y* in Series I. for $x = 6$, 7, and 10. These values locate the supplementary Lines II. and IV., Plate I. They are separated by a small and approximately constant quantity from the Lines I. and III.

A similar discussion of the values for $n = .5$ and .75 will make evident whether or not the addition of KOH beyond 8.13 mol. has any effect. The formation heat of K_2SO_4 is according to Thomsen 31.288 Cal. One half of this, 15.644 Cal., is larger by .96 than the mean result of Exp. 36–39, Series II., which would indicate that heat was absorbed in liberating KOH from its previous state of combination, and hence that the combination of the 9th and 10th mol. in Series I. was accompanied by heat evolution. This, if true, would be an interesting fact; but the question arises, May not the formation heat of K_2SO_4 in Exp. 36–39 be less than 31.288 Cal., this value having been determined for a degree of concentration six times as great? I therefore determined it independently, using, first, the same quantities of KOH and H_2SO_4 as occur in the reaction $n = .5$, and then six times their quantities, the volume 1,000 c.c. remaining the same throughout. In the last case, the proportion is about the same as in Thomsen's experiment. The data are shown in Table IV. At the degree of concentration which corresponds to Exp. 36–39, the formation heat of $\frac{1}{2} K_2SO_4$ is found to be (Exp. 57–61) 14.63 Cal., which agrees with H in Exp. 36–39; while for one sixth this dilution H is found to be 31.26 or 15.63 for $\frac{1}{2} K_2SO_4$; Exps. 53, 54, correspond to Thomsen's conditions.

This proves that the second half of the 9th mol. and the 10th mol. in Series I. are not in chemical combination, or, at least, that there is no evidence of it in the thermal phenomena. In other words, the heat disturbance ceases when 8.13 mol. KOH have been added, as indicated in Line I., Plate I.

As dilution was found to affect the determination of the formation heat of K_2SO_4, it became desirable to test its influence upon the resultant H of Series I., in which this formation heat is the principal element. To do this the reaction heat of 6 mol. KOH on 1 of alum was determined, the absolute amount of substance undergoing change in the standard volume, 1,000 c.c., being only one fourth the quantity used in Exp. 23–26, Series I. These data are recorded in Table V. The mean result of the five experiments is 29.26 Cal., in place of 30.66 by the previous experiments.

It seems not improbable, in view of these facts, that the tendency of the Line III., Plate I., to rise between $x = 1.5$ and $x = 5.1$, may be due to the increase in the amount of substance undergoing change in the unit of volume.

The complexity of the thermochemical results thus far described made evident the necessity of a sharper definition of the chemical changes actually taking place in the calorimeter. The study of these constitutes the second part of this paper.

PART II.

General Method. — It would seem that the most direct method of obtaining evidence as to the exact chemical change would be to determine the composition of the various precipitates produced in the calorimetric experiments. The impossibility, however, of washing them without changing their composition, indicated rather the analysis of the filtrate from them as the preferable method. Either one determines only the total change in the distribution of constituents between the soluble and insoluble portions of the system.

The method pursued was the following: 50 c.c. of alum solution, containing five grammes of the crystallized salt, were made up to a little less than 125 c.c. The required quantity of KOH solution was also made up to about the same volume. These two solutions were then thoroughly mixed, the volume of the mixture made up accurately to 250 c.c. (T 20° C.), again well shaken, and thrown upon a dry filter, the filtration being hastened in some instances by using the pump. From the filtrate separate portions of 50 c.c. each were taken, in which were made duplicate determinations of SO_3 and Al_2O_3, and in several instances of K_2O. The SO_3 was determined, of course, by precipitation with $BaCl_2$; the Al_2O_3, by precipitation with NH_3; and the K_2O was weighed as sulphate after the removal of Al_2O_3. The proportion of constituents and water is the same as in the calorimetric experiments, the scale being simply reduced to one fourth.

Analyses somewhat similar have been made by S. U. Pickering* of the precipitates obtained from aluminic sulphate by addition of varying quantities of Na_2CO_3. His method was to determine the SO_3 and Al_2O_3 in the precipitate itself after thorough washing, although he recognized the fact that its composition was changed by the operation. This would be a serious objection to the use of this method for the purposes of this investigation, although less so in his experiments undertaken from a different standpoint. Our results, so far as they cover the same points, do not conflict in the general direction of their indications, although quantitatively they differ somewhat.

Mills also has determined simply the amount of Al_2O_3 precipitated from alum solution by varying quantities of Na_2CO_3.†

It should be noted that the method of this investigation gives no evidence as to the degree of hydration of the precipitate; that point I am obliged to pass by.

In the first experiment of this series (Exp. A) the method was applied in blank to a solution of alum, no KOH being added. The results obtained were:

Al_2O_3	= .1080 grm.	SO_3	= .3321 grm.
	= .1074		= .3326
Mean	= .1077	Mean	= .3324

As these correspond to 1 grm. alum taken, multiplying by 100 converts them into per cents. Correcting for the volume of pipettes and flask makes them respectively 10.90 and 33.64. Adding to these the determinations of K_2O and H_2O, made by separate experiments, makes the complete analysis of the alum used as follows:

---

* Chemical News, xlv. 121, 133, 146.

† Journal of Chem. Society, [2,] xli. 341.

	Found.	Cal.
Al_2O_3	10.90	10.76
SO_3	33.64	33.75
K_2O	9.94	9.93
H_2O	45.64	45.56
	100.12	100.00

It is evident that the difference between the results of A and of corresponding results of subsequent experiments in which precipitation does occur, gives the amount of Al_2O_3 and SO_3 in the precipitate. The final results of each experiment are reckoned as parts of Al_2O_3 in 100 parts of anhydrous precipitate, and as parts of Al_2O_3 precipitated out of 100 parts of Al_2O_3 present in the total system. The following is an example of a calculation in full: —

	Al_2O_3.	SO_3.
A =	.10766 grm.	.33231
D =	.0689	.31134
Precipitate =	.03876	.02097

$$\text{Anhydrous precipitate} = \frac{.03876 \times 100}{.03876 + .02097} = 64.89\%\ Al_2O_3.$$

$$Al_2O_3 \text{ of precipitate} = \frac{.03876 \times 100}{.10766} = 36.00\% \text{ of total } Al_2O_3.$$

The data of this series of experiments are recorded in Table VI. The quantity of KOH varies, as will be seen, from 1.5 to 8 molecules.

Before discussing the results, I describe another series made to reverse, as it were, the conditions of the former.

Fifty c.c. of alum solution were taken as before, and to this ten molecules KOH added, and the whole made up to a little less than 125 c.c. Sulphuric acid solution, containing quantities of H_2SO_4 proportional to 1.5, 2, 2.5, and 4 molecules, was added, and the mixture brought accurately to 250 c.c. (*T* 20°), thoroughly shaken, filtered, and the filtrate analyzed as usual. The only variation was in Exp. *T*, when 5 mol. HCl were used in place of 2.5 H_2SO_4, and this will be more particularly discussed in a subsequent publication. The data of these experiments are recorded in Table VII.

The calculation of the composition of the precipitate is similar to that in the preceding series, except that account must be taken of the SO_3 added.

In three experiments, viz. *H*, *T*, and *S'''* (in *H* and *T* the total amount of precipitate was at its maximum), the K_2O in the filtrate was determined. The full calculated amount being found, it was deemed unnecessary to determine it at other points, since it evidently formed no part of the precipitate.

Discussion. — The results of the first two series are graphically expressed in Lines V., VI., VII., and VIII., Plate II. In Line V., $x =$ number of molecules of KOH added, and $y =$ per cent of total Al_2O_3 found in the precipitate. While in Line VII., $x =$ the same, but $y =$ parts of Al_2O_3 in 100 parts of anhydrous precipitate. Continuing Line V. beyond $x = 1.5$ and $x = 8$ toward the axis of x indicates $x = 1.13$ and $x = 8.13$ as the probable points respectively of initial and final precipitation. The line reaches its maximum at $x = 4.8$, making the precipitation of the Al_2O_3 complete at this point.

Line VII. shows that the first precipitate is the least basic, containing only 64% of Al_2O_3; that from $x = 1.5$ to $x = 4$ there is apparently a slight increase of basicity, but that from $x = 4$ to $x = 4.8$ the increase is more rapid; that between $x = 4.8$ and $x = 6$ the rapidity of change is still greater; that at $x = 6$ it drops back again, leaving a precipitate free of SO_3 at $x = 7$. It will be noticed that $x = 4.8$ and $x = 6$ are salient points in these lines, as they are in Lines I. and III., expressing the thermal phenomena.

The points in Line VI., $x = 5$, 6, and 7, are obtained from Exp. *N*, *O*, and *T*, by making x the number of molecules of KOH left unneutralized by the H_2SO_4 added. It will be seen that they approximate closely to the corresponding points in Line V., the difference being probably within the limits of experimental error. This evidently means that, when the same amount of free KOH is present, the same precipitate is obtained, whether it come from adding KOH to alum, or from neutralizing the excess of KOH in the alkaline solution of Al_2O_3 obtained by adding 10 KOH to alum. This result was unexpected, and suggested at once the possibility of a chemical equilibrium existing between the constituents of the soluble and of the insoluble portions of the system. To test this idea, Exp. *P* was made, using 4 mol. H_2SO_4. Assuming that 4 mol. KOH out of the ten added are uncombined with H_2SO_4, the 4 mol. H_2SO_4 now added would neutralize them, leaving an excess of 2 mol. H_2SO_4, and making a system, neglecting the K_2SO_4, constituted of 1 mol. Al_2O_3 and 2 H_2SO_4, the same which we suppose to exist when 2 mol. KOH are added to 1 mol. alum. Putting $x = 2$, therefore, the results of Exp. *P* give the points *P* in the Lines VI. and VIII., which approach at least the corresponding points in V. and VII. Regarding this as a further indication of an equilibrium, I varied the experiment in the following manner (Exp. *Q*): The usual 50 c.c. of alum solution were taken, 6 mol. KOH added, and the whole made up to 250 c.c. Another portion of 50 c.c. alum solution was then taken, and made up to nearly 250 c.c. The two solutions thus prepared were then mixed, made up to 500 c.c., thoroughly shaken, filtered, and portions of 50 c.c. taken from the filtrate for analysis, as usual. The total system here is evidently the same in the proportion of its constituents (water included) as would be obtained by mixing 1 mol. alum and 3 mol. KOH in a volume of 250 c.c. At the same time, we can calculate from Exp. *I*, Table VII., what would be the composition of the precipitate, assuming that it remained the same as produced by 6 mol. KOH in the first mixture, increased only by the remaining 9.47% of the total Al_2O_3 of the first portion; the KOH uncombined with H_2SO_4 in that portion taking SO_3 from the second portion of alum, but causing no increase of precipitate since it is equivalent to only about .14 mol. KOH. The precipitate thus calculated would contain 50% of the total Al_2O_3 of the system, and have a composition of 95.29% Al_2O_3 to 4.71% of SO_3. This gives the crossed points *Q* ($x = 3$). But actual analysis of the filtrate gives for the precipitate the results recorded in *Q*, Table VIII., and the points *Q* in the Lines VI. and VIII. This shows that the initial distribution of constituents between the soluble and insoluble portions of the system has changed completely, approaching that obtained by adding to 1 mol. alum 3 mol. KOH. The change in this case consists only in an increase of SO_3 in the precipitate.

Another experiment was then made (Exp. *R*) by mixing in similar manner (1 alum + 6 KOH) in 250 c.c. and (1 alum + 1.5 KOH) in 250 c.c.; making a total system equivalent to 1 alum + 3.8 KOH in 250 c.c. Calculating as in *Q*, from Exp. *B* and *I*, the initial composition of this mixed precipitate, and on the assumption that the unneutralized .1 mol. KOH of the 6 mol. KOH is added to the 1.5 mol. in the second portion, we obtain the crossed points *R* ($x = 3.8$). Analysis of the filtrate, on the other hand, gives the points *R* ($x = 3.8$) in the Lines VI. and VIII., which likewise shows a very considerable change in the precipitate, and a close approach to the system obtained by adding 3.8 mol. KOH to 1 mol. alum. In this case the change is more complex than in *Q*, consisting in the precipitate acquiring both Al_2O_3 and SO_3. In other words, the equilibrium has moved the crossed point *R* up to the point *R* in VI., and the crossed point *R* down to *R* in VIII.

The results already described indicate unmistakably the existence of the equilibrium; but, to vary the evidence still more, Exp. S', S'', and S''' were made, as follows: —

Aluminum was dissolved in KOH solution and the KOH exactly neutralized by HCl, independent experiments having proved that the precipitate thus obtained is free of acid. The volume of this mixture having the freshly precipitated hydrate in suspension was brought up to 250 c.c. Fifty c.c. of alum solution (= 5 grm. alum) were then added, the whole made up to 500 c.c. and thoroughly mixed. Before filtering, portions of 50 c.c. each were withdrawn with a pipette, care being taken to insure the uniform distribution of the suspended precipitate by constant stirring. In these portions the precipitate was redissolved by HCl and the total Al_2O_3 of the system determined. The remainder of the mixture was filtered as usual, and portions of 50 c.c. of its filtrate taken for the usual determinations of SO_3 and Al_2O_3. The differences between the total Al_2O_3 and SO_3 and the Al_2O_3 and SO_3 found in the filtrate give the composition of the precipitate. In S' the amount of Al_2O_3 added as precipitate was 1.12 times that added as alum, making a proportion of 2.12 mol. Al_2O_3 to 3 mol. SO_3 in 500 c.c. of volume; equivalent to 1 Al_2O_3 and 1.4 SO_3 in approximately 250 c.c. This so far as relation between Al_2O_3 and SO_3 is concerned, should be equivalent to 1 alum + 3.2 KOH. Using therefore the analytical results of S', Table VIII., and making $x = 3.2$, we obtain the dotted points S', Plate II., approximating closely to the values otherwise obtained; whereas had the precipitate remained unchanged it would have been 100% Al_2O_3 and contained 52.82% of the total Al_2O_3. These values are represented by the crossed points S'. The change consists mainly in acquiring SO_3.

Exp. S'' is similar, the only variation being in the quantity of precipitated Al_2O_3 added. The results are shown in the points S'' ($x = 2.5$); whereas the crossed points S'' indicate what would have been the results had the precipitate remained unchanged. Here, too, the change is in acquiring SO_3.

Still another experiment, S''', was made, varying again the quantity of Al_2O_3 added. The actual results are shown in the points S''' ($x = 2$), and the initial precipitate in the crossed points, S'''. Here it is apparent that the change consists in gaining SO_3 and losing Al_2O_3.

The proof of equilibrium is indubitable, the initial precipitate gaining or losing Al_2O_3 or SO_3 as may be necessary to bring about the characteristic distribution of constituents for the given conditions. It is also apparent that K_2SO_4 plays no part, and may be considered as practically outside the system, since its presence in quantity varying from less than one molecule to more than ten molecules has not disturbed the leading phenomenon.

Another fact may be noted here. The corresponding points in the Lines V., VI., VII., and VIII., that lie to the right of $x = 5$, approximate closely, probably within the limits of experimental error. To the left of $x = 5$, the divergence is greatest, but the difference in every instance lies on the side of approach to the Lines V. and VII. from the initial points, never going beyond. The probable explanation of this lies in the fact that, in all the experiments yielding the Lines V. and VII., also the points of the other lines to the right of $x = 5$, the system in its initial state is homogeneous. While in the remaining experiments, with the single exception of Exp. *P*, it is non-homogeneous (liquid and solid). It is not strange, then, that this non-homogeneity exercises a retarding influence upon the equilibrium. It is rather a matter of surprise that it should not prove more of an obstacle than it does.

Effect of Temperature, Time, and Dilution on the Equilibrium.

Temperature often exerts an influence in reactions such as we have been describing, and to test its effect in this instance is the object of the three following experiments, E', E'', and E'''. In the first place two successive experiments were made as nearly alike as possible, in order to measure the probable variation in the final results of a single experiment. I give the details in full. The solutions were prepared in the usual manner, 4 mol. KOH being added to 1 mol. alum. The temperature of the room in both experiments was about 23° C., but the contents of flasks before bringing up to standard volume and before taking out portions of 50 c.c. were cooled, as in previous experiments, to 20°. The results were as follows: —

	E'.		E''.	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
Found in 50 c.c. I. =	.0174 grm.	.28221	.0159	.28203
II. =	.0174	.28210	.0162	.28190
Mean =	.0174	.28216	.0161	.28197

	E'. Al_2O_3.	*E'*. SO_3.	*E''*. Al_2O_3.	*E''*. SO_3.
A =	.10766 grm.	.33231	.10766	.33231
E' =	.0174	.28216	.0161	.28197
Precipitate =	.09026	.05015	.09156	.05034

	E'.	*E''*.
Anhydrous precipitate =	64.28% Al_2O_3	64.52% Al_2O_3
=	35.72% SO_3	35.48% SO_3
Precipitate =	83.84% of total Al_2O_3	85.05% of total Al_2O_3

It will be seen that the SO_3 determinations do not differ appreciably more than the duplicate determinations of SO_3 in the same solution; while the amounts of Al_2O_3 obtained, differ by more than a milligramme, one part in seventeen. So in another instance, .2893 and .2899 grm. SO_3 were obtained in two experiments entirely distinct from the beginning. It would almost seem that the equilibrium were more sharply defined with reference to SO_3 than to Al_2O_3. Yet it should be borne in mind that the amounts of SO_3 actually weighed are always large, .28 grm. or more, while the amounts of Al_2O_3 weighed were as low as .01 grm., and hence the experimental determination of SO_3 is less affected by error than that of Al_2O_3.

The final results being dependent on the ratio between differences, small compared with the quantities actually measured, considerable latitude of variation must be allowed.

The experiment was then repeated, *E'''*, the only variation being that, after the flask was filled to 250 c.c. (at 21°), it was heated to about 50–55° for twenty-five minutes, then turned into a large beaker with glass cover and heated fifteen minutes more, and finally boiled two or three minutes. The liquid on the cover was rinsed off with the solution, and the whole thrown while boiling hot upon a dry filter, which was covered during the ten minutes of filtration. The filtrate was then cooled to 20°, and portions of 50 c.c. taken as usual for analysis. The loss of water by evaporation could not have been great, and would not affect the ratio between Al_2O_3 and SO_3. The results were:

	Al_2O_3.	SO_3.
I. =	.0148	.30473
II. =	.0148	
Mean =	.0148	.30473

This makes a precipitate containing 86.25% of the total Al_2O_3, with a composition of 77.10% Al_2O_3 and 22.90% SO_3. The precipitate at the temperature of boiling has, therefore, lost considerable SO_3, while the ratio of the Al_2O_3 precipitated to the total has not much changed.

Exp. E^{IV}. A second variation was made to test the influence of dilution on the equilibrium, since many of the experiments already described indicate that water plays a part in the reaction besides that of a mere solvent. Alum and KOH in the same quantity as in E', E'', and E''' were mixed, and the solution made up to 1,000 c.c., instead of 250, making the absolute quantity in unit of volume one fourth what it was in the preceding experiments. Of the filtrate, portions of 100 c.c. were taken, instead of 50, and the quantities of SO_3 and Al_2O_3 found were multiplied by two in order to make them comparable with the others. The results were:

	Al_2O_3.	SO_3.
I. =	.0162	.28570
II. =	.0160	.28578
Mean =	.0161	.28574

This indicates a precipitate containing 85.05% of total Al_2O_3, and of composition 66.29% Al_2O_3 and 33.71% SO_3.

Dilution also has tended to diminish SO_3 in the precipitate without changing the proportion of Al_2O_3 precipitated.

Is the equilibrium a function of time also? To answer this a mixture was prepared (Exp. E^{V}) at the same time as E', and in precisely the same manner. But instead of filtering at once as in E', the mixture was allowed to stand in a closed flask at the temperature of the room for seven days, and then filtered as in E', and the filtrate analyzed. The result was:

	Al_2O_3.	SO_3.
I. =	.0152	.28210
II. =	.0146	.28217
Mean =	.0149	.28214

This makes a precipitate containing 86.12% of the total Al_2O_3, and in composition 64.89% Al_2O_3 and 35.11% SO_3, or practically the same as in E'. Here, too, is to be seen the close agreement in quantity of SO_3 and the greater variation in Al_2O_3.

This experiment was suggested by the fact that the basic filtrates obtained by adding one or more molecules of KOH, and removing the precipitate, yield a second precipitate on standing, the length of time apparently depending on the degree of basicity. This second precipitate is also produced in a few minutes by boiling or by adding a considerable quantity of water. Exp. E^{V} is therefore interesting as showing that time does not affect the equilibrium while the original precipitate remains in the system.

CONCLUSION.

It is clear, from the evidence herein set forth, that in the reaction which has been the subject of investigation we have another instance of chemical equilibrium or mass reaction, and the question at once arises, What is the cause of it? Without attempting to answer this definitely at present, we suggest the probability that it may be due to the progressive dissociation by water of basic compounds of Al_2O_3 and SO_3 on the one hand, and of potassic aluminate on the other. It would appear from Exp. S', S'', and S''', that $Al_2O_3 \cdot 3\ SO_3$ must itself be partly dissociated in water solution, and it is not improbable that the matter may be still further complicated by the dissociation of another substance formed from the products of decomposition of the first. I hope to obtain definite evidence upon this point, by continuing a line of investigation already begun. That the basic sulphates of alumina are dissociated, is apparently indicated by the fact already cited, that the filtrates in experiments *B* to *H* yield a second precipitate on heating, diluting, or standing some length of time. While the crystallized potassic aluminate to which Fremy assigns the formula, $K_2O \cdot Al_2O_3 \cdot 3\ H_2O$, decomposes on the addition of water with the separation of aluminic hydrate.

However that may be, it is evident, (1.) that the reaction between alum and KOH is not by any means as represented in what may be called the ideal equation cited in the beginning of this paper, but that it is much complicated by secondary reactions which render it entirely unsuitable for the determination of the formation heat of the sulphate and other compounds of alumina, although the numerical error introduced by its use may not be great; and (2.) that these secondary reactions are of the nature of chemical equilibriums or mass reactions, the distribution of the constituents of the system about the line of solubility being a function of temperature, volume (i. e. dilution), and total mass of constituents.

TABLE I.

1 Alum + n KOH.

$A = B = 500. \quad d = 8.5. \quad f = 47655.4.$

No. of Exp.	n.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	$h = H \div n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
1	0.5	16.66	17.275	16.96	.060	2.86	5.72	2.85	5.69
2	0.5	16.4575	17.2225	16.833	.0595	2.84	5.67		
3	1.0	16.6675	17.2925	16.973	.1195	5.70	5.70	5.72	5.72
4	1.0	16.57	17.52	17.037	.1205	5.74	5.74		
5	1.5	16.70	17.0675	16.878	.1695	8.08	5.39	8.09	5.39
6	1.5	16.826	17.73	17.27	.1700	8.10	5.40		
7	2.5	17.02	18.073	17.538	.287	13.68	5.47	13.58	5.43
8	2.5	16.6075	17.04	16.818	.283	13.49	5.39		
9	2.5	16.545	17.40	16.965	.285	13.58	5.43		
10	4.5	17.08	17.93	17.497	.513	24.45	5.43	24.42	5.43
11	4.5	16.525	17.16	16.836	.514	24.50	5.44		
12	4.5	17.44	18.255	17.84	.510	24.31	5.40		
13	4.8	16.18	17.0525	16.609	.5335	25.42	5.30	25.79	5.37
14	4.8	17.2125	17.845	17.522	.548	26.12	5.44		
15	4.8	17.37	18.5775	17.965	.535	25.50	5.31		
16	4.8	16.4325	17.80	17.107	.548	26.12	5.44		
17	5.12	17.03	16.92	16.971	.594	28.31	5.53	28.39	5.55
18	5.12	17.06	17.68	17.363	.5945	28.33	5.53		
19	5.12	16.78	17.75	17.257	.5955	28.38	5.54		
20	5.12	16.17	17.0075	16.581	.599	28.55	5.58		
21	5.5	16.69	17.46	17.068	.632	30.12	5.48	30.14	5.48
22	5.5	16.49	17.35	16.912	.633	30.17	5.49		
23	6.0	19.5825	20.15	19.86	.640	30.49	5.08	30.66	5.11
24	6.0	19.84	20.5075	20.167	.633	30.17	5.03		
25	6.0	16.66	17.84	17.241	.6515	31.05	5.18		
26	6.0	16.6925	17.62	17.148	.6495	30.95	5.16		
27	6.5	16.2375	16.8825	16.553	.647	30.83	4.74	30.83	4.74
28	6.5	16.62	17.895	17.248	.6495	30.95	4.76		
29	6.5	16.445	17.705	17.066	.644	30.69	4.72		
30	7.0	19.15	19.72	19.429	.621	29.59	4.23	29.59	4.23
31	10.0	16.9725	18.01	17.483	.617	29.40	2.94	29.27	2.93
32	10.0	16.46	17.84	17.14	.610	29.07	2.91		
33	10.0	16.62	17.74	17.171	.619	29.50	2.95		
34	10.0	19.26	20.34	19.791	.6115	29.14	2.91		
35	10.0	19.1975	20.21	19.696	....	29.22	2.92		

TABLE II.

(1 Alum + 10 KOH) + n H_2SO_4.

$A = B = 500.$ $d = 8.5.$ $f = 47655.4.$

No. of Exp.	n.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	$h = H \div n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
36	.50	19.2575	20.49	19.865	.305	14.54	29.07	14.68	29.36
37	.50	19.41	20.445	19.919	.311	14.82	29.64		
38	.75	17.81	19.14	18.465	.4575	21.80	29.07	21.83	29.10
39	.75	17.8175	19.0075	18.404	.4585	21.85	29.13		
40	1.00	18.19	19.5525	18.862	.628	29.93	29.93	30.05	30.05
41	1.00	18.21	19.725	18.957	.633	30.17	30.17		
42	1.50	17.92	18.305	18.107	.998	47.56	31.71	47.39	31.60
43	1.50	17.9675	18.9375	18.444	.991	47.23	31.49		
44	2.00	17.8975	18.98	18.43	1.340	63.86	31.93	63.55	31.77
45	2.00	19.094	19.65	19.366	1.3415	63.93	31.97		
46	2.00	17.605	19.0375	18.311	1.319	62.86	31.43		
47	2.20	17.82	19.0575	18.43	1.4575	69.46	31.57	69.28	31.49
48	2.20	18.22	18.53	18.37	1.450	69.10	31.41		
49	3.00	17.80	18.665	18.225	1.785	85.07	28.36	85.07	28.36

TABLE III.

(1 Alum + 4.8 KOH) + 1.2 KOH.

$A + d = 1008.5.$ $B = 124.96.$ $f = 47655.4.$

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	Mean H.
	°	°	°	°	Cal.	Cal.
50	18.08	18.67	18.144	.086	4.10	3.83
51	17.57	17.87	17.602	.073	3.48	
52	17.0475	16.565	16.993	.082	3.91	

TABLE IV.

$2\,KOH + H_2SO_4$. $A = B = 500$. $d = 8.5$.

No of Exp.	n = grm. of H_2SO_4.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times \frac{1008.5 \times 98}{n = \text{grm. } H_2SO_4}$.	Mean H.
		°	°	°	°	Cal.	Cal.
53	6.8071	17.6925	18.45	18.064	2.1435	31.12	31.26
54	6.8071	17.64	18.9075	18.264	2.1385	31.05	
55	6.227	14 62	15.43	15.018	1.9895	31.58	
56	6.227	15.27	15.96	15.608	1.972	31.30	
57	1.0391	17.1725	19.1275	18.138	.312	29.43	29.26
58	1.0391	18.30	19.45	18.866	.3065	28.91	
59	1.024	14.1675	14.8950	14.524	.311	29.76	
60	1.024	14.845	15.485	15.158	.307	29 38	
61	1.024	14.31	15.6275	14.959	.301	28.81	

TABLE V.

1 Alum + 6 KOH. $A = B = 500$. $d = 8.5$.

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times \frac{1008.5 \times 948.24}{5}$.	Mean H.
	°	°	°	°	Cal.	Cal.
62	18.76	19.83	19.287	.1505	28.82	29.26
63	19.01	20 07	19.532	.148	28.34	
64	19.13	19.77	19.443	.157	30.06	
65	19.54	19.9075	19.718	.152	29.10	
66	19.9925	20.22	20.101	.1565	29.96	

TABLE VI. — ANALYSES.

1 Alum + x KOH.

Exp.	x.	Grm. Al_2O_3 found in 50c.c. of Filtrate.	Grm. SO_3 found in 50c.c. of Filtrate.	Al_2O_3 in 100 pts. of Prec.	SO_3 in 100 pts. of Prec.	K_2O in 100 pts. of Prec.	Per cent of total Al_2O_3 in Prec.
A	0.	.10766	.33231	0.	0.	0.	0.
B	1.5	.09738	.32651	63.93	36.07	....	9.55
C	2.0	.08310	.31883	64.56	35.44	....	22 81
D	2.5	.0689	.31134	64.89	35.11	....	36.00
E	4.0	.01995	.28588	65.39	34.61	....	81.47
H	4 79	.0	.28967	71.63	28.37	0.	100.
I	6.0	.0102	.32699	94.82	5.18	....	90.53
J	6 5	.0294	.32927	96.26	3.74	....	72 69
K	7.0	.0547	.33174	100.	0.	....	49.19
L	8.0	.1019	.33231	100.	0.	....	5.35

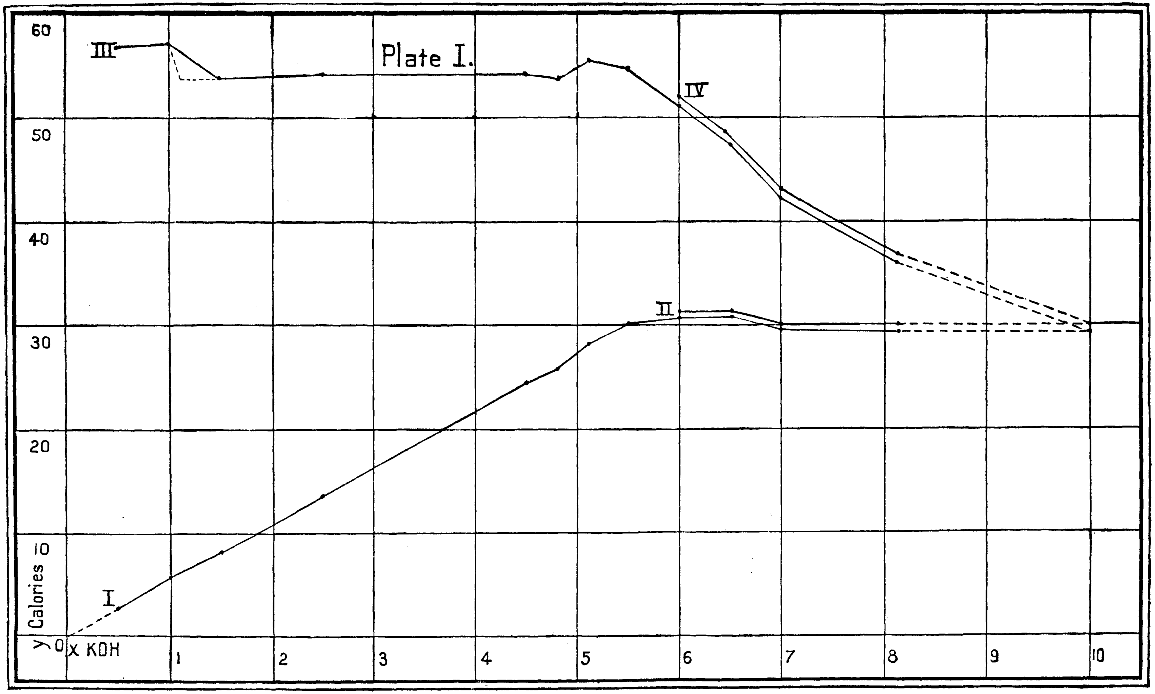

Plate I.

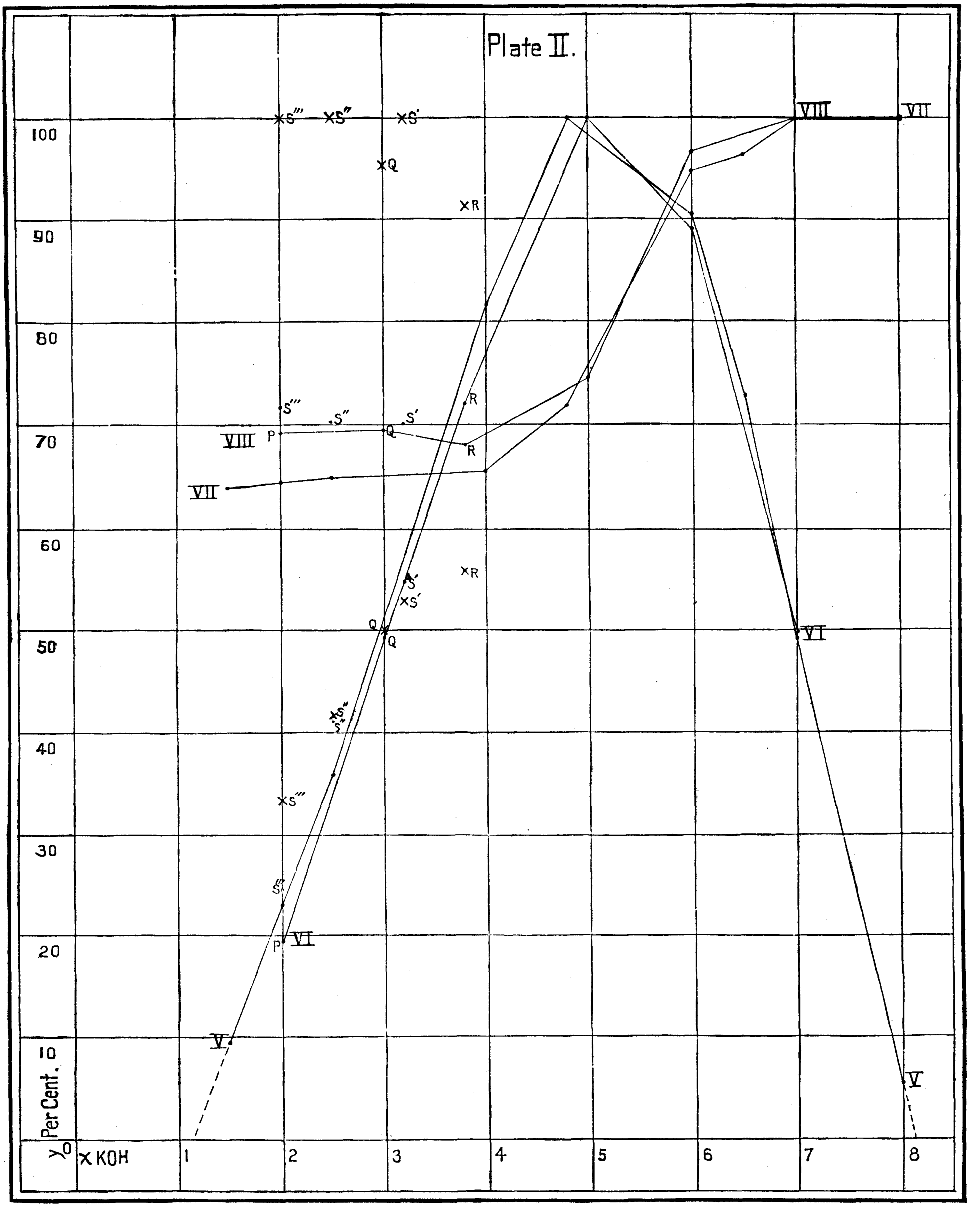

Plate II.
100
90
80
70
60
50
40
30
20
10
Per Cent.
y 0
× KOH
1
2
3
4
5
6
7
8
×S‴
×S″
×S′
×Q
×R
VIII
VII
S‴
S″
S′
P
Q
R
R
VIII
VII
×R
S′
×S′
Q
Q
VI
×S‴
S‴
P
VI
V
V

TABLE VII. — ANALYSES.

(1 Alum + 10 KOH) + $x\,H_2SO_4$.

Exp.	x.	Grm. Al_2O_3 found in 50c.c. of Filtrate.	Grm. SO_3 found in 50c.c. of Filtrate.	Al_2O_3 in 100 pts. of Prec.	SO_3 in 100 pts. of Prec.	K_2O in 100 pts. of Prec.	Per cent of total Al_2O_3 in Prec.
N	1.5	.0540	.45788 cal. .45679 found.	100.	0.	....	49.84
O	2.0	.0119	.50011 cal. .49673 found.	96.59	3.41	....	88.95
T	2.5	.0	.33231 cal. .29512 found.	74.33	25.67	0.	100.
P	4.0	.0867	.66969 cal. .66036 found.	69.20	30.80	....	19.47

TABLE VIII. — ANALYSES.

1 Alum + x KOH.

Exp.	x.	Grm. Al_2O_3 found in 50c.c. of Filtrate.	Grm. SO_3 found in 50c.c. of Filtrate.	Al_2O_3 in 100 pts. of Prec.	SO_3 in 100 pts. of Prec.	K_2O in 100 pts. of Prec.	Per cent of total Al_2O_3 in Prec.
Q	3.0	.0547	.30898	69.42	30.58	....	49.19
R	3.8	.0300	.29598	68.13	31.87	....	72.13
S′	3.2	.0516	.13951	70.11	29.89	....	54.78
S″	2.5	.0543	.15017	70.33	29.67	....	41.11
S‴	2.0	.0608	.15835	71.74	28.26	0.	24.57